STANFORD UNIVERSITY LIBRARY
DEC 10 1928

The Polarization of Binary Liquid Mixtures

STANLEY OWEN MORGAN

STANFORD UNIVERSITY LIBRARIES

3781
P95M

UNCLASSED
Dissertation

The Polarization of Binary Liquid Mixtures

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

STANLEY OWEN MORGAN

Accepted by the Department of Chemistry,
November 1, 1927.

THE POLARIZATION OF BINARY LIQUID MIXTURES. I. THE POLARIZATION OF SOLUTIONS OF SOME CHLOROBENZENES IN BENZENE AND HEXANE[1]

Some years ago it was recognized that the calculation of the electric moments of molecules from dielectric constants might provide valuable aid in solving the complex problems of molecular structure. An approximate method of calculation was devised and applied to data on pure substances already existing in the literature to obtain the moments of a large number of molecules.[2]

It was evident, however, that many molecules which were surrounded by strong fields of force did not lend themselves to this calculation. The experimental work, which was then being initiated in the Palmer Physical Laboratory, was, therefore, directed to the measurement of the dielectric constants and densities of liquid mixtures in which a molecule with a strong field of force could be surrounded by molecules with weak fields. It is our aim to use these data not only for the calculation of electric moments and the study of molecular structure, but also for the investigation of the effect of the force fields of the molecules upon one another in causing molecular association and deviations from ideal behavior.

Theoretical

As the nature of the electric moment and its relation to molecular structure has been discussed in the papers already referred to, only the equations immediately necessary will be given here. The molar polarization P of a substance in which the molecules are free to assume a perfectly random orientation may be represented by the Debye equation,[3] written in the following form

[1] Papers based upon the data of the present contribution were presented before the Physical and Inorganic Division and before the Organic Division of the American Chemical Society in Philadelphia, September, 1926. The results of the measurements upon the substituted benzene compounds have been applied in a study of the structure of the benzene ring, Smyth and Morgan, *J. Am. Chem. Soc.* **49**, 1030 (1927).

[2] (a) Smyth, *Phil. Mag.*, **45**, 849 (1923); (b) **47**, 530 (1924); (c) *J. Am. Chem. Soc.* **46**, 2151 (1924); (d) **47**, 1894 (1925).

[3] Debye, *Physik. Z.*, **13**, 97 (1912); "Handbuch der Radiologie (Marx)," Akademische Verlagsgesellschaft M. B. H., Leipzig, **1925**, VI, p. 619.

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4\pi}{3}N\gamma + \frac{4\pi N}{9k}\frac{\mu^2}{T} \qquad (1)$$

in which ϵ = the dielectric constant; M = the molecular weight; d = the density; N = the number of molecules in a gram molecule = 6.061×10^{23}; γ = the molecular polarizability; k = the molecular gas constant = 1.372×10^{-16}; μ = electric moment of a single molecule; and T = the absolute temperature. $(4\pi/3)N\gamma$ is the polarization due to shifts of charges in the molecule induced by the external field. It is commonly calculated as the molar refraction for light of infinite wave length, $MR_\infty = [1-\lambda_0^2/\lambda^2]\ [(n^2-1)M]/[(n^2+2)d]$, where n is the index of refraction for light of wave length λ, and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. The quantity thus calculated by extrapolation from the visible region takes account only of the electronic shifts induced, and is, therefore, designated as P_E, but atoms and groups of atoms or radicals may shift under the influence of an external field in such a way as to contribute somewhat to the polarization.[4] We may, therefore, write $(4\pi/3)N\gamma = P_E + P_A$, where P_A, the difference between P_E and the total polarization induced in the molecules may be termed the atomic and radical contribution to the polarization. Setting $(4\pi N/9k)\ (\mu^2/T)$, the contribution of the moments of the molecules oriented by the external field, $= P_M$, we have $P = P_E + P_A + P_M$.

When the molecules are rigidly bound in the solid state and, therefore, unable to orient themselves in an applied field, $P_M = 0$. By determining the polarization P in the solid state, calculating P_E from optical data, and setting $P_M = 0$, Errera[5] has obtained values of P_A for a number of substances. When the molecules in a liquid affect one another to such an extent that they are not oriented at random in the absence of an external field, the expression for P_M may no longer be expected to hold. If the molecules are oriented in such a way that the axes of their electric doublets tend to point in the same direction, P_M is increased, while if these doublets tend to oppose one another, it is decreased. This arrangement of the doublets relative to one another may be anything from a very slight orientation of the molecules to an association in the form of molecular complexes.

The molar polarization of a mixture of two substances, 1 and 2, is given by the expression[3]

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\frac{c_1M_1 + c_2M_2}{d} = c_1P_1 + c_2P_2 \qquad (2)$$

in which c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual compo-

[4] Ebert, *Z. physik. Chem.*, **113**, 1 (1924); **114**, 430 (1925).

[5] Errera, *Physik. Z.*, **27**, 764 (1926).

nents. As $c_1 = 1-c_2$, it is evident that P_{12} is a linear function of c_2 when P_1 and P_2 are constant. If P_1 is constant but P_2 varies with concentration the latter may be calculated by writing the equation in the form

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1 \qquad (3)$$

In the study of binary mixtures, one may choose a liquid 1, such as benzene or hexane, the molecules of which have no moment and may be described as non-polar, and, for liquid 2, a substance[2c] the molecules of which have large moments and will be referred to as polar. In such mixtures, P_1 may be assumed to be approximately constant, since its value is equal to $P_E + P_A$, which are dependent upon intramolecular behavior and vary little with concentration. The variation of P_2 with concentration may then be taken as an indication of the character and extent of the molecular orientation or association of substance 2.

The equation of Debye was criticized by exponents of the older quantum theory, but applications of the newer quantum mechanics to simple polyatomic molecules have given equations from which results practically identical with those of the Debye equation may be obtained and Van Vleck[6] has recently given a general proof of the equation on the basis of the new mechanics. Experimental investigations have shown[7] that, in a simplified form, the equation represents admirably the temperature variation of the dielectric constants of a number of dipole gases but, presumably, because of lack of complete freedom of the molecules, it has not been found generally satisfactory when applied to a pure dipole liquid.

Apparatus and Procedure

The measurements of dielectric constant were made with a capacity bridge, which was used in preference to newer methods involving coupled oscillating circuits because of the frequent failure of the latter to distinguish between capacity and conductance, which failure may introduce a serious error into apparently precise results. It is probable, however, that a newer circuit of established accuracy may be used in later measurements.

As the apparatus possessed certain novel features, a diagram is given in Fig. 1, in which electric shields are represented by dotted lines. The oscillator, bridge and detector were each in separate galvanized iron boxes, fitting closely against one another and grounded. The oscillator tube was a Western Electric 216-A type operated with 135 volts on the plate and giving a direct current in the plate circuit of approximately 30 milliamperes. The three coupling coils (L_1, L_2, L_3) were wound beside one another on the same fiber core. The setting of the variable condensers (C_1 and C_2) across the fixed grid and plate inductances (L_1 and L_2) determined the frequency of the oscillations,

[6] Van Vleck, *Phys. Rev.*, **29**, 727 (1927); **30**, 31 (1927).

[7] (a) Jona, *Physik. Z.*, **20**, 14 (1919); (b) Zahn, *Phys. Rev.*, **24**, 400 (1924); (c) Smyth and Zahn, *J. Am. Chem. Soc.* **47**, 2501 (1925); (d) Sänger, *Physik. Z.*, **27**, 556 (1926); **28**, 455 (1927).

5×10^5 cycles corresponding to a wave length of 600 meters being adopted as suitable for the bridge and checked occasionally by means of a wave meter. The condensers (C_3 and C_4, C_5) across the power and detector coils (L_3 and L_4, L_5) were for tuning, by means of which it was possible to increase two- or three-fold the deflection of the galvanometer used as null instrument for a given capacity change in either arm of the bridge. The power was brought from the oscillator to one corner of the bridge by a heavy, shielded wire, the circuit being completed by grounding the opposite corner of the bridge. In order to maintain the symmetry of the bridge, this power lead was carried beneath the bottom of the box containing the bridge and brought vertically up to the corner shown between R_1 and R_2. The bridge consisted of two resistance arms, R_1, R_2, of 1000 ohms each, specially wound non-inductively on the same Bakelite

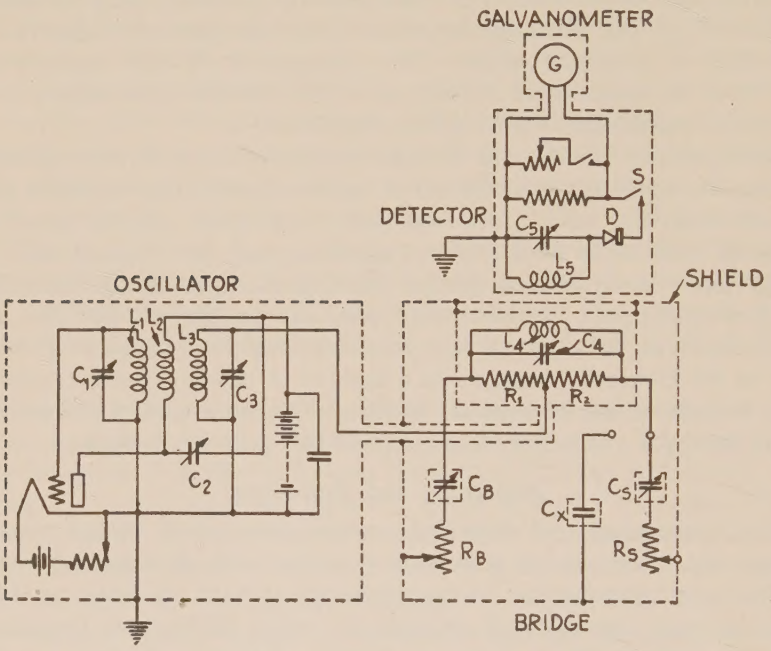

Fig. 1.—Capacity bridge.

cylinder and shielded from the rest of the bridge, and two capacity arms, the balancing condenser C_B, a 2000 $\mu\mu$f shielded air condenser, and the standard condenser C_S, a General Radio Company type 222 precision instrument of 1500 $\mu\mu$f capacity. These condensers were connected to the grounded shield through General Radio Company decade resistance boxes, R_B and R_S, non-inductively wound. The resistance in series with C_B was used to balance any conductance in the measuring cell C_x, which could be connected in parallel with C_S, while that in series with C_S was rarely used, having been inserted largely with the object of maintaining the symmetry of the bridge as far as possible. The ends of R_1 and R_2, remote from one another and forming opposite corners of the bridge were connected through a small honey-comb coil, L_4, loosely coupled through a grounded electrostatic shield to another coil, L_5, current through which was rectified by a crystal detector, D, and passed through a Leeds and Northrup high sensitivity galvanometer G, minimum deflection of which indicated balance of the bridge. A switch, S, which could be operated without opening the box, was used to close the

detector circuit. The galvanometer was critically damped and a variable shunt was used to protect the galvanometer while bringing the bridge approximately to balance.

A balance of the bridge was obtained when the capacity and conductance were the same in each arm. When the conductance in the opposite arms was different there was a current flowing in the galvanometer, even though the capacity in both arms was the same.

The method of operation was to vary the standard condenser and the balancing resistance until practically zero current was obtained in the galvanometer, both conductance and capacity being then balanced. The condenser containing the liquid to be measured was then connected in parallel with the variable standard condenser and the bridge balanced again by varying the standard condenser and balancing resistance. The capacity of the measuring condenser was equal to the change of the variable standard condenser required to bring the bridge back to balance. With the liquids used in this work, it was unnecessary to change the balancing resistance by more than a few tenths of an ohm.

The measuring condenser C_x consisted of two concentric gold-plated brass cylinders closed at both ends, separated by a distance of 1 mm. on the sides, and insulated from each other and held rigidly by quartz disks set in bushings at the ends. A slightly larger gold-plated cylinder with a cover served as container. Twenty-five cc. of liquid were required to fill this container and the air capacity of the condenser was 34 $\mu\mu$f.

The capacity of the measuring condenser was made up of two parts, the fixed capacity due to the leads and insulation, which did not vary with the dielectric constant of the liquid in the cell, and the capacity between the plates, which was directly proportional to the dielectric constant of the liquid in the condenser. The condenser was calibrated by determining its capacity filled with air and again filled with a liquid whose dielectric constant was well known. The calibrating liquid was benzene, for which a mean value of $\epsilon = 2.273$ at 25° was adopted from the work of Isnardi,[8] Graffunder[9] and Lertes.[10]

Ether, toluene, chloroform and carbon tetrachloride were also measured with a view to calibration and the agreement obtained with the most probable values for the dielectric constants of these substances was satisfactory, but, as the benzene value appeared to be the most accurate, it seemed best to rely wholly on it.

The precision condenser C_S, after being fixed in position in the bridge, was recalibrated in terms of a fixed capacity, that of the empty measuring cell serving as a convenient unit, and this calibration was checked from time to time.

The densities of the liquids were determined with an Ostwald-Sprengel pycnometer, the ends of which were fitted with caps to prevent evaporation. For measurements at 0°, the cell and pycnometer were immersed in cracked ice and water, and, at 25 and 50°, in carefully regulated thermostats. The probable error of the dielectric constant measurements was 0.5% and of the density determinations 0.03%.

Preparation of Materials

The hexane used was Eastman Kodak Company petroleum hexane, b. p. 65–70°. The first lot was treated with acid and alkaline permanganate as recommended by Castelli and Henri[11] and then fractionated. The middle fraction differed from the unpurified material so little in its

[8] Isnardi, *Z. Physik*, **9**, 153 (1922).

[9] Graffunder, *Ann. Physik*, **70**, 225 (1923).

[10] Lertes, *Z. Physik*, **6**, 257 (1921).

[11] Castelli and Henri, *Bull. soc. chim. biol.*, **6**, 299–302 (1924).

dielectric properties that, in the work which followed, the untreated hexane was used.

Merck's crystallizable benzene was shaken three times with concentrated sulfuric acid and then with water. It was dried over phosphorus pentoxide and fractionated.

The monochlorobenzene was shaken several times with concentrated sulfuric acid, then with water, dried over fused calcium chloride and fractionated.

The dichlorobenzenes were Eastman Kodak Company products. The ortho and meta isomers were fractionated under reduced pressure, only the middle fraction being used. The para compound was crystallized twice from ethyl alcohol and thoroughly dried over calcium chloride.

Results

Table I gives the experimentally determined dielectric constants and densities of the liquid mixtures at 0, 25 and 50°, together with the values

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF BINARY MIXTURES

Mole fraction of	ϵ			d			P_{12}		
	0°	25°	50°	0°	25°	50°	0°	25°	50°
C_6H_5Cl in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0786	2.710	2.621	2.518	0.9214	.8973	.8713	31.80	31.58	31.13
.1988	3.140	2.994	2.853	.9485	.9227	.8963	37.28	36.80	36.16
.4007	3.879	3.659	3.443	.9986	.9712	.9441	45.09	44.45	43.70
.6020	4.650	4.332	4.050	1.0435	1.0178	.9907	52.00	51.14	50.37
.7048	5.039	4.665	4.339	1.0663	1.0393	1.0125	55.10	54.20	53.30
1.000	6.088	5.628	5.226	1.1272	1.1006	1.0737	62.84	62.06	61.25
o-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0205	...	2.453	2.373	....	.8837	.8570	...	29.34	29.10
.054	2.873	2.724	2.607	0.9243	.9022	.8792	33.97	33.05	32.44
.1156	3.331	3.153	2.998	.9621	.9328	.9063	39.11	38.54	37.93
.2015	4.023	3.777	3.561	1.0016	.9748	.9476	46.06	45.34	44.67
.5010	6.520	5.988	5.547	1.1367	1.1094	1.0826	64.22	63.50	62.73
1.000	11.130	9.930	8.900	1.3251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0372	2.497	2.414	2.342	0.9184	.8916	.8648	29.22	28.97	28.80
.1008	2.719	2.629	2.533	.9494	.9234	.8966	32.61	32.40	32.04
.2703	3.283	3.130	2.989	1.0314	1.0033	.9761	40.48	40.02	39.48
.6837	4.552	4.254	3.997	1.2014	1.1702	1.1427	56.47	55.67	54.76
1.000	5.403	5.039	4.703	1.3085	1.2799	1.2523	66.80	65.90	64.80
p-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.1354	2.372	2.323	2.266	0.9673	.9407	.9135	28.34	28.49	28.37
.1483	2.389	2.341	2.276	.9735	.9466	.9198	28.70	28.79	28.65

Mole fraction of	ϵ 0°	ϵ 25°	ϵ 50°	d 0°	d 25°	d 50°	P_{12} 0°	P_{12} 25°	P_{12} 50°
.3860	...	2.359	2.313	....	1.0555	1.0280	...	30.92	31.00
.6741	...	...	2.369	....	...	1.1421	...	...	34.16
.7335	...	...	...	....	....	1.1703	...	...	...
C_6H_5Cl in C_6H_{14}									
0.0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0293	2.060	1.989	1.922	.6990	.6761	.6528	32.47	31.87	31.28
.0792	2.201	2.122	2.039	.7177	.6940	.6707	35.13	34.59	33.83
.1470	2.419	2.312	2.221	.7430	.7191	.6952	38.89	38.07	37.43
.2903	2.870	2.727	2.543	.7981	.7748	.7505	45.14	44.26	42.61
.4979	3.690	3.453	3.249	.8860	.8601	.8353	52.98	51.94	50.92
.7540	4.824	4.467	4.153	1.0027	.9770	.9511	59.28	58.19	57.13
.8477	5.370	4.953	4.602	1.0502	1.0222	.9962	61.24	60.36	59.40
1.000	6.088	5.628	5.226	1.1278	1.1008	1.0741	63.03	62.26	61.62
o-$C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0255	2.100	2.035	1.966	.7037	.6805	.6572	33.50	33.14	32.58
.0739	2.382	2.292	2.190	.7327	.7084	.6848	39.09	38.51	37.63
.1320	2.783	2.630	2.503	.7684	.7425	.7184	45.73	44.66	43.73
.3406	4.370	4.030	3.744	.8935	.8715	.8463	63.30	61.66	60.29
.5881	6.498	5.873	5.384	1.0527	1.0238	.9978	74.88	73.75	72.60
1.000	11.130	9.930	8.900	1.3251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0204	2.024	1.969	1.900	.7056	.6818	.6587	31.57	31.36	30.30
.0245	...	...	...	.7061	.6840	.6608	...	...	...
.0684	2.168	2.087	2.014	.7318	.7085	.6850	34.64	34.03	33.40
.2084	2.602	2.480	2.337	.8140	.7926	.7682	42.24	41.21	39.64
.4324	3.270	3.090	2.948	.9477	.9235	.8980	51.22	50.07	49.36
1.000	5.403	5.039	4.703	1.3085	1.2799	1.2523	66.80	65.90	64.80

of the polarization, P_{12}, calculated by means of equation (2). Typical curves showing the variation of these quantities with the composition of the mixture are given in Figs. 2, 3 and 4. For the sake of brevity, the actual values calculated for P_2, the molar polarization of the polar substance, at the different concentrations are omitted but the results obtained for benzene solutions at 50° are plotted in Fig. 5. The P_2 curves obtained for the solutions in hexane were similar in character to those for the benzene solutions, which are shown in preference to the former because *p*-dichlorobenzene was measured only in benzene. The values of P_2 at infinite dilution at 25° obtained by extrapolation to zero concentration ($c_2 = 0$) of the polar substance are given in Table II as P_∞, together with the values of P_E calculated from data in "International Critical Tables" in agreement with the calculations of Errera,[6] P_A obtained by Errera for the dichlorobenzenes, P_M calculated as $P_M = P_\infty - (P_E + P_A)$, and the electric moment calculated from P_M. Solid monochlorobenzene has not been investigated but an approximate value, 3.3, may be calculated for P_A

from results to be described in our next paper. This value is, therefore, inserted here and used to obtain P_M and μ.

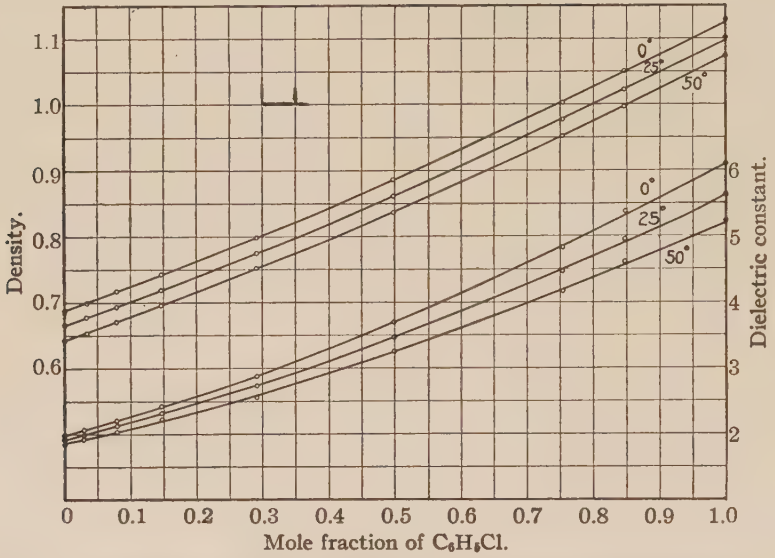

Fig. 2.—Densities and dielectric constants of chlorobenzene–hexane mixtures.

TABLE II

POLARIZATION CONTRIBUTIONS AT 25° AND ELECTRIC MOMENTS OF THE CHLORO-BENZENES

	P_∞	P_E	P_A	P_M	$\mu \times 10^{18}$
C_6H_5Cl	83.6	29.9	3.3	50.4	1.56
o-$C_6H_4Cl_2$	145	34.4	5.8	104.8	2.25
m-$C_6H_4Cl_2$	84.3	34.6	4.4	45.3	1.48
p-$C_6H_4Cl_2$	37.8	34.8	3.4	0	0

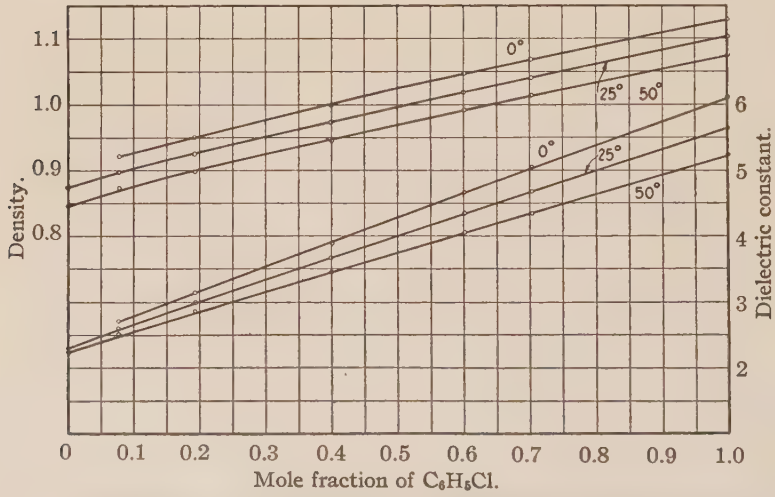

Fig. 3.—Densities and dielectric constants of chlorobenzene–benzene mixtures.

Discussion of Results

The value for the moment of monochlorobenzene agrees well with the figure 1.58×10^{-18} recently published by Höjendahl[12] and by Williams and Krchma,[13] who, being unable to take into account the small quantity P_A, obtained a slightly high value. It also differs by less than the possible error from the value, 1.52×10^{-18}, obtained by the more accurate method to be described in Part II of this series. All the values of the moment in Table II are, of course, slightly lower than those first published[1] when no data were available for the calculation of P_A. The values of the polarizations of pure *o*- and *m*-dichlorobenzene are in satisfactory agreement with those of Errera and that for P_∞ of the para compound is identical with Errera's value. For this latter compound, P_M is given as 0 instead of the

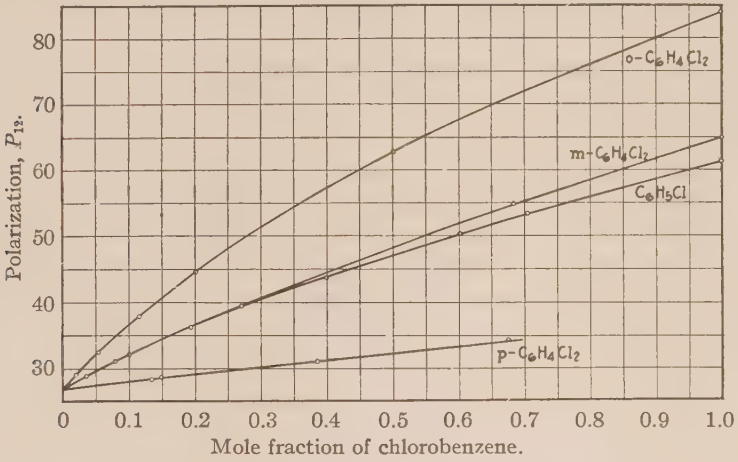

Fig. 4.—Polarization (P_{12}) of mixtures of chlorobenzenes with benzene at 50°.

figure −0.4 actually obtained, which is less than the probable error and has no apparent physical significance. The values for P_∞ of the ortho and the meta compound and consequently of the moments are distinctly higher than those obtained by Errera, whose extrapolation was made at but one temperature and based upon measurements in only one solvent.

The curves (Figs. 2 and 3 show typical curves) representing the variation of the dielectric constant and the density with the mole fraction c_2 of the polar substance are, in some cases, very nearly linear, but the dielectric constant curves usually possess marked curvature. The departure from linearity of both the dielectric constant and the density curves evidently depends upon the character not only of the polar substance but also of the non-polar. For a given set of mixtures at different temperatures,

[12] Höjendahl, *Nature*, **117**, 892 (1926).

[13] Williams and Krchma, *J. Am. Chem. Soc.*, **49**, 1676 (1927).

the density curves run much more nearly parallel than the dielectric constant curves, which spread apart with increasing content of the polar substance because of the high temperature coefficient of the latter indicated by equation (1). In Fig. 4 *p*-dichlorobenzene, which has no electric moment, is the only substance showing a linear variation of P_{12} with c_2 as required by equation (2) if P_1 and P_2 are constant and independent of c_2. The departure from linearity of the other curves is attributable to decrease in P_2, the polarization of the polar substance, because of increase

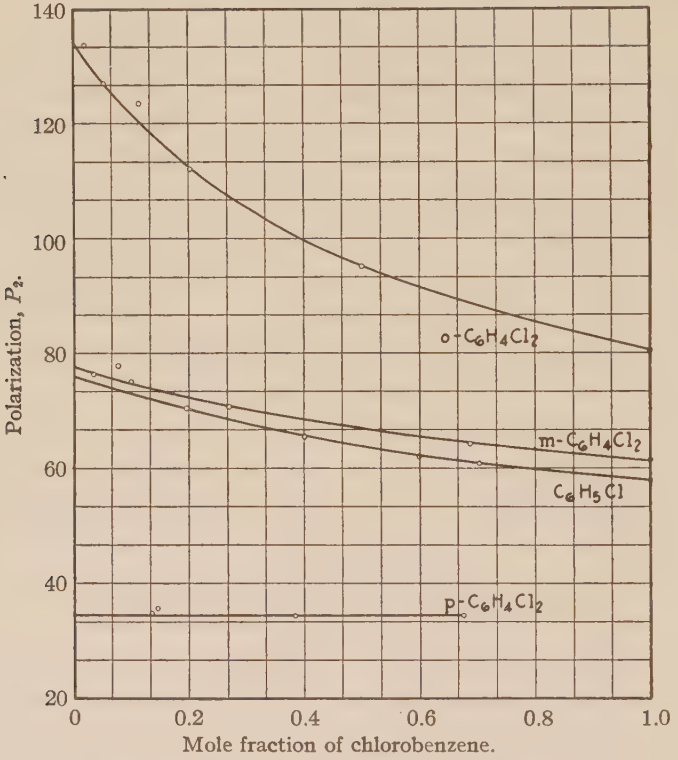

Fig. 5.—Polarization (P_2) of chlorobenzenes in benzene solutions at 50°.

in molecular orientation with increasing concentration. Monochlorobenzene and *m*-dichlorobenzene, which have nearly equal moments, have very similar curves, that for the latter lying a little higher in the more concentrated region because of its greater chlorine content, which gives a higher value for MR_∞. The relations are clear in Fig. 5, in which the P_2 curve for the para compound is a horizontal straight line showing independence of concentration when the moment is zero. For the other compounds, P_2 decreases rapidly with increasing concentration, particularly

in the dilute region, the decrease being greatest in the case of the ortho compound which has the largest moment. The values at different temperatures, which have been omitted for the sake of brevity, show that P_2 decreases with rising temperature more rapidly in the dilute solutions than in the concentrated, where increasing thermal agitation gives increased freedom to the molecules, which can thus orient more freely in the applied field.

It may be concluded that the molecules of the chlorobenzenes tend to orient themselves in such a way that neighboring doublets oppose one another, thereby decreasing the polarization. This effect is greater, the greater the moment of the molecule, the lower the temperature and the smaller the distance between the doublets, that is, the greater the concentration. Measurements upon solutions of acetic acid in benzene and in ether, which, because of their preliminary character and uncertain interpretation, are not included in the present paper, indicate that, as might be expected, not only the magnitude of the field of force around the single molecule but also steric influences and highly localized valence forces may play an important part in determining the behavior of the molecules.

II. THE TEMPERATURE DEPENDENCE OF THE POLARIZATION IN CERTAIN LIQUID MIXTURES[1]

As the results reported in Part I showed that the effect of polar molecules upon one another in dilute solution varied greatly with concentration and with temperature, it was evident that accurate determinations of dielectric constant and density over a wide range of temperature were needed.

Apparatus

The apparatus described in Part I was modified, although the same capacity bridge with the same wave length of 600 meters was used. The Western Electric 216-A tube in the oscillator was replaced by a 5-watt 104-DW power tube, upon the plate of which 250 volts were applied by means of a high speed motor generator. This increased the accuracy of the bridge balance by supplying more current. The measuring cell used in the earlier work was replaced by a condenser of approximately 200 $\mu\mu$f. capacity, which greatly reduced the relative error of a capacity measurement. Since the capacity of this cell when filled with a liquid of high dielectric constant was greater than that of the precision condenser which was used to measure it, a 1000 $\mu\mu$f. variable air condenser of the same type as that used in the balancing arm of the bridge was so arranged that, by means of interchangeable brass rods dipping into cups filled with mercury, it could be connected in series with the cell or in parallel with the precision condenser or could be totally disconnected. When the capacity of the cell was too great to be measured by direct substitution on the precision condenser, this variable air condenser was set at a convenient value, measured on the precision condenser, and then connected in series with the cell. The capacity of the cell and condenser, thus reduced by the series con-

[1] A paper based upon the results of the present contribution was presented before the Physical and Inorganic Division of the American Chemical Society in Richmond, April, 1927.

nection, was measured on the precision condenser and the capacity of the cell alone then calculated.

The measuring cell (Fig. 1) was designed in such a way as to have large electrical capacity, small internal volume and small temperature lag. It was made up of three concentric platinum cylinders (A), with diameters 1.95, 1.80 and 1.64 cm., respectively, open at the ends. The outer and inner cylinders, which were 9.2 cm. long, were connected together and to ground while the middle cylinder, which was 8 cm. long, was centered between them and held at a distance of 0.05 cm. from them by small blocks of mica placed at the top and bottom. The entire condenser was enclosed in a vessel consisting of two concentric glass tubes sealed together at top and bottom, the outer tube being but slightly larger than the outer platinum cylinder and the inner tube fitting inside the innermost platinum cylinder. The leads, which were platinum wires welded to the cylinders, were brought out through heavy capillary tubes (B, B′), spread to a distance of 8 cm. from one another to reduce the mutual inductance and capacity of the leads, the ends of which were sealed into the bottoms of mercury filled cups (C, C′) to make connections with the bridge.

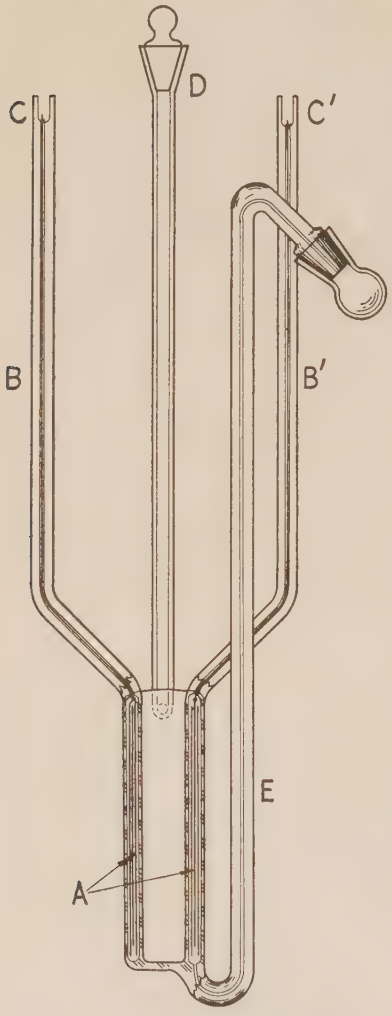

Fig. 1.—Measuring condenser.

These tubes (B, B′), as well as the inlet and outlet tubes (D and E), extended 22 cm. above the cell, which could, therefore, be immersed well below the surface of a constant temperature bath. The cell, which held only 18 cc., was filled through the inlet tube D, which was provided with a ground glass stopper, and was emptied by applying air pressure to D and forcing the liquid through the capillary outlet tube E, which could be closed with a ground glass cap over the end. The cell was normally kept in a vertical position and, if necessary, could be filled and emptied without removal from the constant temperature bath. It was dried by means of a current of filtered, dry air. As the cross section of the cell was a ring, it was in contact with the bath liquid both inside and out. The grounded outer and inner cylinders of the condenser served as shielding for the shorter cylinder between them. Stray, fixed and lead capacities were so reduced that the capacity which depended upon the substance in the cell was 96% of the total when the cell contained air. The variation of the air capacity of the condenser over the temperature range -90 to $+60°$ was no greater than the error of the measurement. The cell was standardized as in the earlier work by determining its capacity when filled with air and with benzene ($\epsilon = 2.273$ at 25°), the standardization being checked from time to time.

The constant temperature bath[2] was a Pyrex Dewar tube, 18″ tall by 4″ inside diameter, which, for temperatures below −90°, was filled with petroleum ether, between −90 and +90°, with toluene, and, above +90°, with kerosene. Immersed in the bath was a small copper cylinder into which liquid air could drip through a small, straight tube and out of which the evaporated air could escape through a spiral tube. A vacuum jacketed siphon carried the liquid air to this cooling device from a stoppered 2-liter Pyrex Dewar flask, pressure being developed by the evaporation of liquid in the flask and regulated by attachment to a tube passing through the stopper of capillary tubes of varying bore and length. The copper cylinder was surrounded by a small heating coil which was used to raise the temperature of the bath when desired.

The temperatures were measured with a Leeds and Northrup platinum resistance thermometer fitted with compensating leads, the resistances being determined with a Callendar bridge. The thermometer was calibrated at +100, 0 and −95.5°, the melting point of toluene, and was later checked against the freezing point of a pure sample of normal heptane which had been previously determined with a calibrated thermocouple. The end of the thermometer was placed inside the hollow ring of the cell and, in every case, the temperature was held constant to within 0.1° for ten or fifteen minutes before making a measurement. At least two capacity readings differing from one another by less than 0.03% were made at each temperature in order to eliminate any possibility of error due to temperature variation. Densities were measured with a pycnometer (Fig. 2) somewhat similar in form to that used by Isnardi.[3] The bulb, A, which had a volume of about 25 cc., was connected to the stoppered overflow bulb B by the carefully ground joint C. The vessel was filled and hung with the bulb A immersed in the bath. When the liquid in the pycnometer had had time to attain the temperature of the bath, the bulb B was removed and the level of the liquid adjusted to a definite height in the capillary D. The bulb B was then replaced and the pycnometer removed from the bath, allowed to come to room temperature and weighed. Deposition of frost on the cold pycnometer was prevented by immersion in ether while it was warming up. The usual corrections were made in weighing and calibration was effected at different temperatures with toluene and with water. By proper design and grinding of the joints pycnometers were obtained which, when filled with hexane at −90°, tightly stoppered and allowed to come to room temperature, lost only 5 to 10 milligrams in weight on standing for fifteen hours. The probable error in the low temperature density determinations was 0.1% but in the measurements carried out at ordinary temperatures it was not more than 0.03%. The probable error in the dielectric constant measurements was 0.2%, although the relative accuracy within a given series of measurements was usually greater than this.

Fig. 2.—Pycnometer.

Preparation of Materials

Chlorobenzene was prepared in the manner described in the first paper. Pure normal hexane was obtained from the Eastman Kodak Company and treated just as was the petroleum hexane in the earlier investigation. Its refractive index at 20° for sodium light was found to be 1.37527, agreeing within the experimental error with the value 1.37536 given in Landolt-Börnstein "Tabellen" (5th ed.).

[2] Compare Walters and Loomis, *J. Am. Chem. Soc.*, **47**, 2302 (1925).

[3] Isnardi, *Z. Physik*, **9**, 153 (1922).

Ethyl bromide was freshly prepared from alcohol and potassium bromide, shaken once with concentrated sulfuric acid, then several times with water, dried over fused calcium chloride and distilled. Its density, $d_4^{20} = 1.452$, differed from the values found in the literature. It was washed again three times with small quantities of concentrated sulfuric acid, seven times with ice water and dried over fused calcium chloride. It all distilled at 38.5° and had a density, $d_4^{20} = 1.4586$. This value agrees with those given in Landolt-Börnstein "Tabellen," 1.4555 and 1.4569, but differs greatly from the value $d_4^{20} = 1.430$ given in "International Critical Tables." The density measurement has been repeated on other samples of ethyl bromide and the value $d_4^{20} = 1.458$ is believed to be correct.

Chloroform was shaken several times with concentrated sulfuric acid,

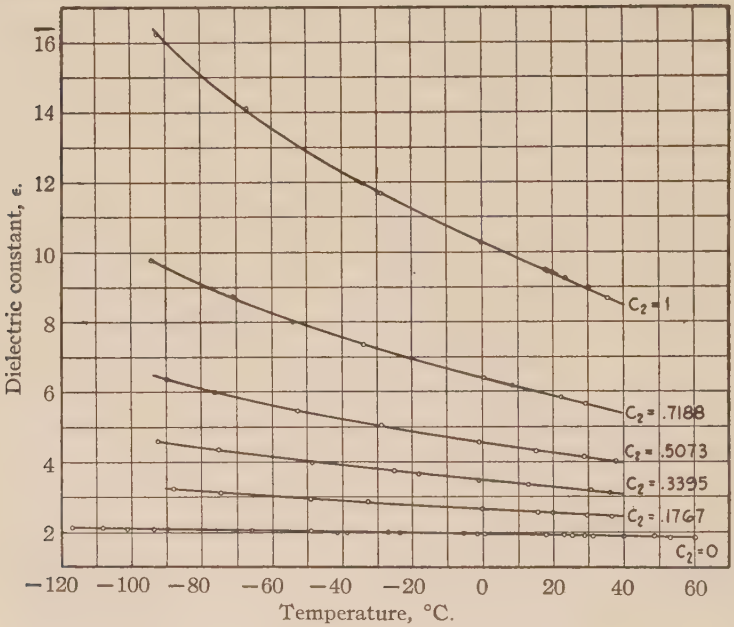

Fig. 3.—Temperature variation of dielectric constants of hexane–ethyl bromide mixtures.

with dilute sodium hydroxide and with water. It was dried over anhydrous potassium carbonate and fractionated.

Results

The dielectric constants and densities of hexane, ethyl bromide, chloroform, chlorobenzene and solutions of the substances in hexane were measured over the entire range of temperatures at which the materials were liquid under atmospheric pressure. The data were plotted against tem-

perature on a very large scale and the values at 10° temperature intervals read off. The values for different mixtures at the same temperature were then plotted against c_2, the mole fraction of the polar substance, ethyl bromide, chloroform or chlorobenzene, as the case might be, and the values for $c_2 = 0.05, 0.1, 0.2, 0.3$, etc., were read off. By means of the equations $P_{12} = (\epsilon - 1)/(\epsilon + 2)\ (c_1M_1 + c_2M_2)/d$, and $P_2 = [(P_{12} - P_1)/c_2] + P_1$, in which ϵ = the dielectric constant, d = the density, c_1 and c_2 = the mole fractions and M_1 and M_2 = the molecular weights, the molar polarization, P_{12}, of the mixtures, and P_2, the polarization of the polar substance, were obtained at the different concentrations and temperatures. The values of P_2 at one temperature were plotted against c_2 and the curve

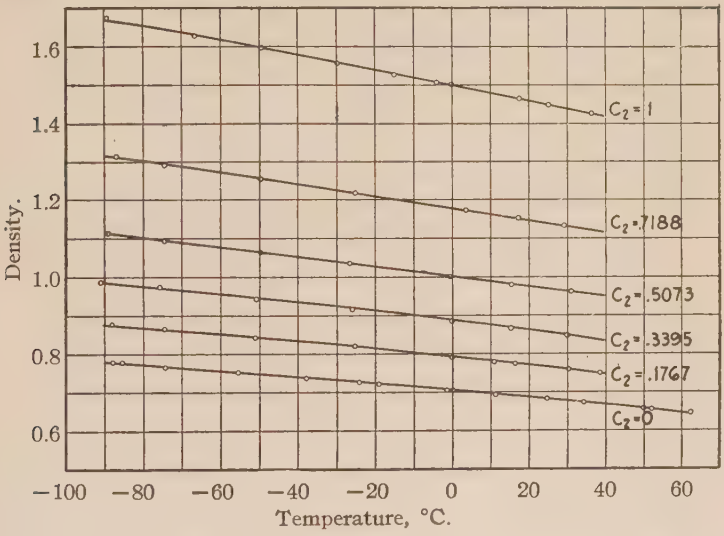

Fig. 4.—Temperature variation of densities of hexane–ethyl bromide mixtures.

was extrapolated to $c_2 = 0$ to obtain P_∞, the polarization at infinite dilution, where the molecules should be oriented at random when no external field is applied. A series of curves at different temperatures gave P_∞ over the entire temperature range within which the mixtures were liquid.

Table I contains the values of the dielectric constant, ϵ, and the density, d, at the actual temperatures of measurement, for the pure liquids, but, for the sake of brevity, omits the measurements on the mixtures. Table II gives for each combination of substances the values of ϵ and d interpolated at 10° intervals for each mixture studied, but omits the data interpolated for $c_2 = 0.05, 0.1, 0.2$, etc. The results shown under $c_2 = 0$ in the hexane–ethyl bromide combination are for petroleum hexane which, as in the earlier work, was used in the mixtures. The constants of this mix-

ture of isomers were, of course, somewhat different from those for the pure normal hexane given in Table I. In Table III, the polarization of both the pure normal hexane and the petroleum hexane are designated as

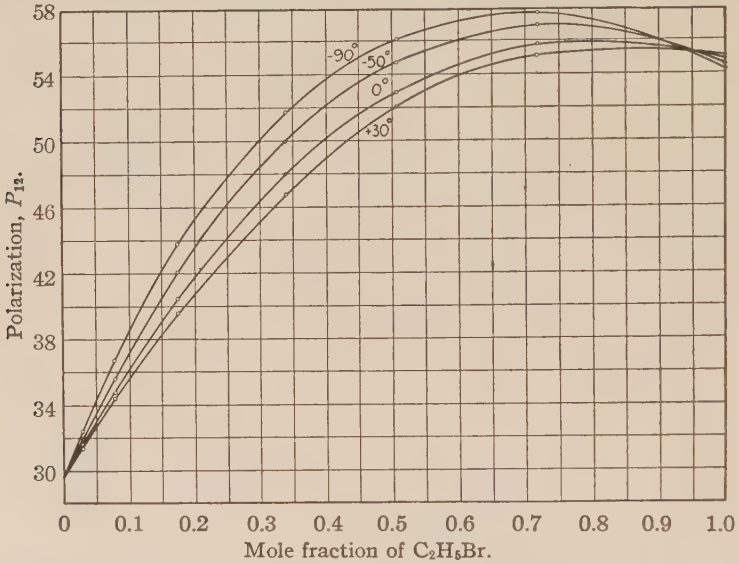

Fig. 5.—Molar polarizations of hexane–ethyl bromide mixtures.

P_1, which is assumed to be independent of concentration. For each of the other substances the polarization of the pure liquid, P_2, is shown beside P_∞, the polarization extrapolated to infinite dilution.

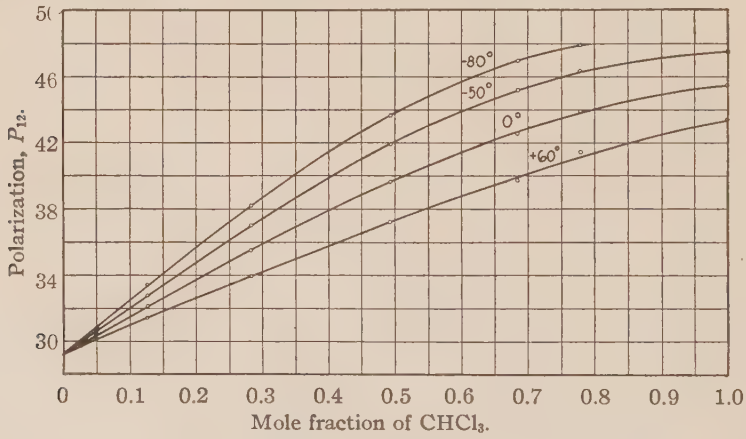

Fig. 6.—Molar polarizations of hexane–chloroform mixtures.

Fig. 3 shows the temperature variation of the dielectric constant of each mixture of petroleum hexane and ethyl bromide, each curve being

designated by the value of c_2, the mole fraction of ethyl bromide, and Fig. 4 shows in similar fashion the temperature variation of the densities. The curves for the mixtures of the other substances which are not shown are similar to these in form. Figs. 5, 6 and 7 show the variation with concentration of the molar polarization of the mixture, P_{12}, at a given temperature. For each set of mixtures curves are given at convenient in-

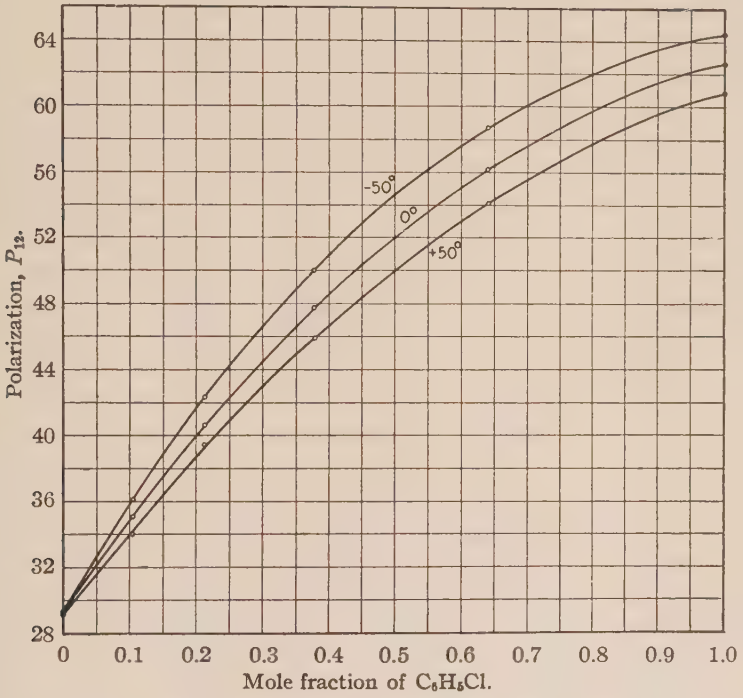

Fig. 7.—Molar polarizations of hexane–chlorobenzene mixtures.

tervals over the entire temperature range. It is hoped that the variation of P_2 with temperature and concentration may be treated in a later paper.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF PURE LIQUIDS

n-Hexane				Ethyl Bromide			
t, °C.	ϵ	t, °C.	d	t, °C.	ϵ	t, °C.	d
−91.3	2.051	−89.5	0.7540	−92.3	16.22	−89.2	1.6737
−89.4	2.050	−77.6	.7442	−66.7	14.10	−66.4	1.6283
−71.6	2.023	−63.6	.7324	−28.6	11.67	−49.0	1.5950
−61.3	2.006	−47.0	.7185	0	10.28	−29.5	1.5572
−57.8	2.003	−29.5	.7035	+18.3	9.49	−14.6	1.5274
−37.0	1.976	−12.7	.6886	+18.5	9.48	− 3.3	1.5050
−19.3	1.948	− 1.3	.6787	+18.7	9.45	0	1.4996
− 0.1	1.918	+10.4	.6686	+20.0	9.40	+17.7	1.4634
+ 9.1	1.907	+15.8	.6664	+23.8	9.25	+25.2	1.4479

TABLE I (*Concluded*)

Chloroform				Chlorobenzene			
t, °C.	ϵ	*t*, °C.	*d*	*t*, °C.	ϵ	*t*, °C.	*d*
+15.0	1.898	+27.5	.6555	+30.3	8.99	+36.6	1.4245
+28.2	1.879	+38.3	.6458	+35.5	8.67		
+39.4	1.863	+50.1	.6325				
+47.1	1.848	+61.2	.6219				
+57.0	1.824	+67.0	.6158				
−62.6	6.810	−61.3	1.6397	−49.0	7.240	−42.7	1.1742
−61.0	6.748	−54.6	1.6271	−45.5	7.150	−24.5	1.1561
−59.7	6.707	−48.7	1.6161	−25.8	6.684	− 3.3	1.1314
−55.6	6.576	−25.0	1.5725	+ 0.1	6.013	0	1.1277
−51.8	6.428	−23.4	1.5696	+18.3	5.662	+18.7	1.1080
−49.6	6.387	− 1.1	1.5282	+22.0	5.593	+46.3	1.0777
−40.5	6.120	0	1.5265	+23.2	5.580	+73.5	1.0475
−22.4	5.703	+24.2	1.4814	+29.2	5.475	+97.2	1.0206
−18.8	5.552	+50.1	1.4308	+47.8	5.174	+103.3	1.0319
−15.0	5.466	+59.8	1.4116	+75.1	4.822	+124.5	0.9914
− 2.2	5.195			+100.0	4.516	+126.0	.9906
+ 4.5	5.078			+100.5	4.460		
+17.2	4.825			+115.5	4.346		
+18.7	4.802			+126.0	4.174		
+35.5	4.520						
+45.8	4.351						
+54.0	4.231						
+58.6	4.163						

TABLE II

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS HEXANE–ETHYL BROMIDE

Mole fraction of C_2H_5Br =	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
t, °C.	Dielectric Constant							
−90	2.078	2.270	2.568	3.240	4.573	6.360	9.60	16.05
−80	2.063	2.245	2.520	3.152	4.416	6.095	9.12	15.15
−70	2.048	2.219	2.476	3.075	4.270	5.856	8.68	14.35
−60	2.033	2.194	2.437	3.002	4.135	5.634	8.28	13.62
−50	2.017	2.170	2.400	2.934	4.006	5.418	7.91	12.95
−40	2.002	2.147	2.365	2.870	3.887	5.217	7.56	12.32
−30	1.987	2.123	2.331	2.808	3.776	5.027	7.23	11.75
−20	1.972	2.101	2.300	2.752	3.667	4.852	6.93	11.22
−10	1.957	2.080	2.270	2.700	3.570	4.690	6.65	10.73
0	1.942	2.059	2.240	2.648	3.476	4.544	6.38	10.27
+10	1.927	2.038	2.211	2.599	3.385	4.407	6.14	9.82
+20	1.912	2.018	2.181	2.552	3.294	4.275	5.91	9.41
+30	1.896	1.997	2.153	2.500	3.200	4.146	5.65	8.98
+40	1.880	1.975	2.124	2.444	3.112	3.985	5.40	8.44
+50	1.862	1.953	2.093					
+60	1.843	1.929						
	Density							
−90	0.7813	0.7973	0.8235	0.8804	0.9880	1.1155	1.3176	1.6752
−80	.7734	.7887	.8140	.8704	.9767	1.1026	1.3020	1.6555

Mole fraction of C_2H_5Br =	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
t, °C.	Density							
−70	.7650	.7800	.8048	.8605	.9653	1.0897	1.2867	1.6358
−60	.7564	.7710	.7956	.8505	.9540	1.0768	1.2717	1.6162
−50	.7478	.7622	.7862	.8405	.9423	1.0640	1.2560	1.5966
−40	.7390	.7533	.7770	.8305	.9306	1.0512	1.2405	1.5776
−30	.7300	.7443	.7677	.8206	.9193	1.0383	1.2255	1.5580
−20	.7210	.7356	.7585	.8106	.9078	1.0256	1.2100	1.5384
−10	.7120	.7266	.7493	.8005	.8963	1.0126	1.1947	1.5188
0	.7032	.7174	.7400	.7906	.8848	1.0000	1.1797	1.4993
+10	.6940	.7082	.7302	.7800	.8735	0.9872	1.1640	1.4790
+20	.6854	.6990	.7204	.7693	.8615	.9743	1.1480	1.4586
+30	.6760	.6897	.7103	.7588	.8495	.9616	1.1313	1.4380
+40	.6668	.6800	.7003	.7480	.8374	.9486	1.1144	1.4164
+50	.6574	.6702	.6900					
+60	.6473	.6600						

Hexane–Chloroform

Mole fraction of $CHCl_3$ =	0.0517	0.1277	0.2862	0.4953	0.6856	0.7803	1.000
t, °C.	Dielectric Constant						
−90	2.201	2.409	....	....	....	....	....
−80	2.177	2.371	2.848	3.710	4.785	5.465	....
−70	2.155	2.335	2.786	3.584	4.582	5.210	....
−60	2.133	2.302	2.726	3.469	4.400	4.984	6.720
−50	2.113	2.271	2.668	3.363	4.234	4.778	6.402
−40	2.092	2.241	2.612	3.265	4.076	4.586	6.100
−30	2.072	2.212	2.560	3.174	3.934	4.406	5.825
−20	2.053	2.186	2.512	3.090	3.802	4.256	5.580
−10	2.033	2.159	2.466	3.010	3.680	4.108	5.356
0	2.014	2.134	2.426	2.937	3.568	3.972	5.150
+10	1.995	2.109	2.387	2.867	3.462	3.843	4.960
+20	1.976	2.086	2.348	2.800	3.360	3.720	4.783
+30	1.957	2.062	2.310	2.736	3.266	3.606	4.614
+40	1.938	2.038	2.270	2.670	3.173	3.496	4.450
+50	1.919	2.012	2.230	2.606	3.076	3.394	4.292
+60	1.900	1.984	2.189	2.544	2.974	3.295	4.140
	Density						
−90	0.8122	0.8580	....	....	....	....	....
−80	.8032	.8484	0.9547	1.1175	1.2955	1.3967	....
−70	.7942	.8388	.9440	1.1053	1.2810	1.3813	1.6560
−60	.7853	.8295	.9333	1.0933	1.2668	1.3660	1.6374
−50	.7763	.8198	.9225	1.0804	1.2525	1.3500	1.6188
−40	.7673	.8102	.9120	1.0685	1.2380	1.3342	1.6000
−30	.7582	.8008	.9008	1.0560	1.2234	1.3188	1.5814
−20	.7488	.7914	.8900	1.0435	1.2087	1.3034	1.5633
−10	.7392	.7818	.8790	1.0303	1.1963	1.2875	1.5445
0	.7304	.7722	.8682	1.0173	1.1800	1.2706	1.5262
+10	.7210	.7623	.8576	1.0042	1.1648	1.2557	1.5080
+20	.7116	.7522	.8462	0.9914	1.1498	1.2398	1.4895
+30	.7013	.7420	.8353	.9784	1.1342	1.2236	1.4704

TABLE II (*Concluded*)

	Density						
+40	.6922	.7317	.8236	.9652	1.1188	1.2073	1.4516
+50	.6823	.7214	.8116	.9517	1.1038	1.1905	1.4315
+60	.6721	.7115	.7998	.9380	1.0888	1.1737	1.4105

HEXANE–CHLOROBENZENE

Mole fraction of C_6H_5Cl =	0.1068	0.2132	0.3798	0.6458	1.000
t, °C.	Dielectric Constant				
−80	2.532	3.053	....	....	....
−70	2.490	2.977	3.848	5.484	....
−60	2.448	2.908	3.730	5.268	....
−50	2.409	2.844	3.620	5.086	7.28
−40	2.371	2.784	3.518	4.882	7.01
−30	2.336	2.728	3.424	4.717	6.758
−20	2.304	2.677	3.336	4.560	6.502
−10	2.273	2.629	3.257	4.415	6.260
0	2.244	2.584	3.180	4.280	6.027
+10	2.214	2.540	3.108	4.156	5.818
+20	2.184	2.497	3.040	4.038	5.633
+30	2.153	2.456	2.977	3.928	5.460
+40	2.120	2.416	2.913	3.827	5.300
+50	2.084	2.377	2.846	3.723	5.150
+60	2.050	2.347	2.777	3.627	5.016
+70		2.300	2.706	3.538	4.888
+80				3.443	
	Density				
−80	0.8140	0.8548	....	....	....
−70	.8050	.8460	0.9166	1.0325	....
−60	.7960	.8368	.9067	1.0225	....
−50	.7868	.8278	.8967	1.0120	1.1838
−40	.7777	.8188	.8868	1.0015	1.1726
−30	.7687	.8096	.8774	0.9914	1.1614
−20	.7597	.8005	.8677	.9810	1.1502
−10	.7505	.7912	.8578	.9704	1.1394
0	.7414	.7815	.8480	.9603	1.1280
+10	.7323	.7723	.8384	.9500	1.1172
+20	.7232	.7632	.8285	.9398	1.1060
+30	.7138	.7532	.8185	.9296	1.0953
+40	.7044	.7434	.8086	.9192	1.0840
+50	.695	.7333	.7983	.9087	1.0732
+60	.685	.7228	.7878	.8980	1.0620
+70		.7124	.7770	.8872	1.0513
+80				.8760	

TABLE III

POLARIZATIONS

	C_6H_{14} Petroleum normal		C_2H_5Br		$CHCl_3$		C_6H_5Cl	
t, °C.	P_1	P_1	P_2	P_∞	P_2	P_∞	P_2	P_∞
−90	29.15	29.57	54.24	143.5	...	..	...	...
−80	29.15	29.63	54.32	138.5	...	62.1	...	106.5
−70	29.15	29.65	54.38	135.0	...	60.2	...	103.0

t, °C.	C_6H_{14} Petroleum normal P_1	P_1	C_2H_5Br P_2	P_∞	$CHCl_3$ P_2	P_∞	C_6H_5Cl P_2	P_∞
−60	29.16	29.66	54.47	131.0	47.85	58.9	...	100.0
−50	29.16	29.69	54.54	127.0	47.42	57.5	64.33	97.0
−40	29.16	29.72	54.60	123.5	46.97	56.0	64.00	94.0
−30	29.20	29.72	54.67	118.5	46.53	54.6	63.70	91.0
−20	29.23	29.76	54.74	114.3	46.14	53.1	63.30	89.3
−10	29.23	29.79	54.84	111.0	45.76	52.3	62.88	87.5
0	29.26	29.81	54.92	107.9	45.42	51.1	62.47	85.5
+10	29.28	29.87	54.98	105.5	45.04	50.0	62.06	83.5
+20	29.29	29.92	55.07	103.3	44.70	49.7	61.74	81.5
+30	29.30	29.91	55.07	100.2	44.35	48.8	61.40	79.0
+40	29.28	29.90	54.82	97.6	44.02	48.3	61.12	77.8
+50	29.23	29.85		95.4	43.63	47.5	60.82	76.8
+60	29.16	29.74			43.30	47.3	60.65	76.0
+70							60.40	

Discussion of Results

The values for petroleum hexane are slightly different from those for the pure normal hexane, but their polarizations are so nearly equal and show such similarity of behavior that the use of the petroleum hexane as an indifferent solvent is justified. In Fig. 3 the almost horizontal curve for $c_2 = 0$ shows the small temperature variation of the dielectric constant of petroleum hexane, but a rapid increase of slope accompanies increase in the ethyl bromide content of the mixture. The density curves, on the other hand, are nearly parallel.

As was observed in the earlier work, the curves in which the values of P_{12}, the polarizations of the mixtures, are plotted against the concentration of the polar substances, show strong deviation from the theoretical linearity, the deviation, as before, being larger, the larger the moment of the polar molecule, the greater the concentration of the polar molecules and the lower the temperature. Thus, the P_{12} curves for chloroform, which has the smallest moment of the three polar substances studied, are nearly straight lines in the dilute region, and the curve for 60° shows only a small departure from linearity throughout its course, but this departure from linearity increases as the temperature is lowered. Chlorobenzene, which has a larger moment, shows a noticeable curvature throughout all the curves, but the curvature increases with decreasing temperature and increasing concentration. The effect upon one another of the dipoles in the ethyl bromide molecules, which have the largest moments of the three considered, is so great that the curves pass through a maximum. As this effect diminishes rapidly with rising temperature, the curves intersect almost at one point, the polarization of the mixture containing 0.95 mole fraction of ethyl bromide being practically independent of temperature. In pure ethyl bromide increasing thermal agitation by increasing the freedom of the molecules from one another's fields does more to facilitate

the orientation of the molecule in an externally applied field than it does to destroy this orientation by the increasing violence of the motion. Thus, the polarization actually increases with rising temperature instead of decreasing as required by the Debye equation, $P = a + b/T$, which should apply when the molecules are free to assume a random orientation. In terms of the quantities discussed in the earlier work, the constant

$a = P_E + P_A$, $b/T = P_M$, and the constant $b = 4\pi N\mu^2/9k$, where
P_E = the polarization due to electronic shifts induced in the molecules
P_A = the polarization due to shifts of atoms or radicals induced in the molecules
P_M = the polarization due to orientation of the dipoles
μ = the electric moment of a single molecule
N = the number of molecules in a gram molecule = 6.061×10^{23}, and
k = the molecular gas constant = 1.372×10^{-16}

As it is apparent that the polarization should be a linear function of $1/T$, the values of both P_2 and P_∞ are plotted against $1/T$ in Fig. 8. All

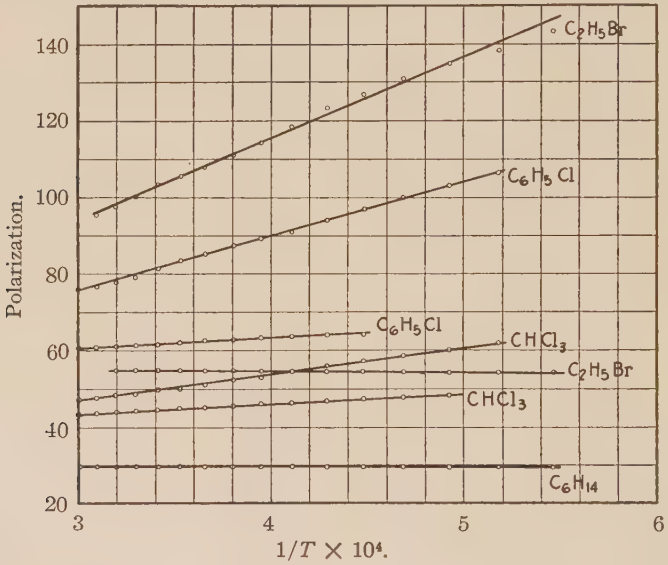

Fig. 8.—Variation of P_2 and P_∞ with $1/T$. (The higher curve for each substance represents P_∞.)

the curves are linear, but the P_2 curve for ethyl bromide gives a negative value of b and the P_2 curves for the other two substances give values of b much lower than those which determine the slopes of the P_∞ curves. The low values of b are due to the orienting effects of the dipoles upon one another, which cause the deviation from linearity of the $P_{1,2} - c_2$ curves. The values of P_∞, to which the Debye equation should apply, vary so much with temperature that the linearity of these curves affords strong evidence in support of the Debye theory.

If the equation is written in the form $PT = a\,T + b$ and the values of PT are plotted as ordinates against T, as abscissas, we should obtain a

straight line of which the slope is a and the ordinate at $T = 0$ is b. In Fig. 9, $P_\infty T$ is plotted for the three polar substances and $P_1 T$ for hexane. The values obtained from these curves for a, b and μ, calculated from b, are given in Table IV, together with the values of $MR_\infty = P_E$, calculated

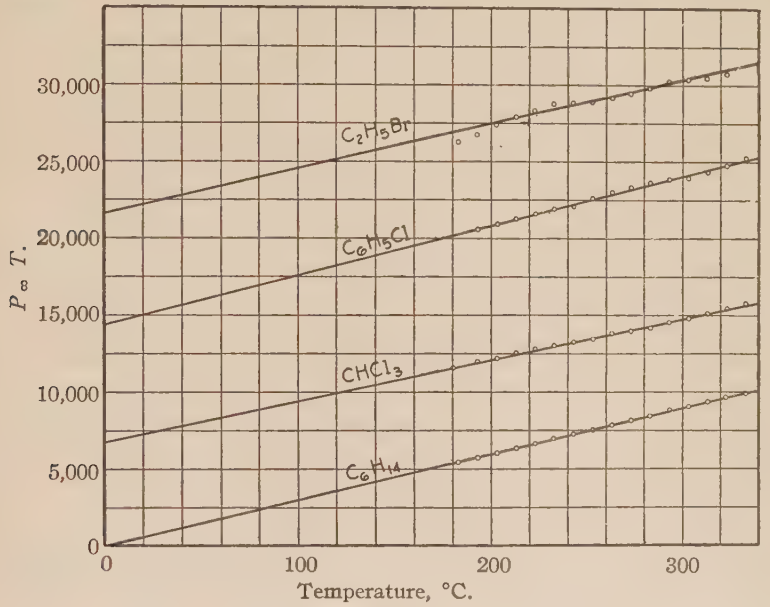

Fig. 9.—Variation of $P_\infty T$ with T.

by extrapolation of refractive index data from the visible region, and values of P_A, calculated from the relation $P_E + P_A = a$.

TABLE IV

VALUES OF FUNDAMENTAL CONSTANTS

	a	P_E	P_A	b	$\mu \times 10^{18}$
C_6H_{14}	29.8	29.20	0.6	0	0
$CHCl_3$	26.6	20.84	5.8	6800	1.05
C_6H_5Cl	33.2	29.93	3.3	14150	1.52
C_2H_5Br	29.5	18.55	(11)	21420	1.86

The very small difference between a and P_E for hexane confirms the value of 0 obtained from the fact that $b = 0$. The value of $\mu = 1.05 \times 10^{-18}$ for chloroform differs from the value 0.95×10^{-18} obtained by Sänger[4] from measurements on the vapor by an amount no greater than that which might arise from the probable errors of the two determinations. This agreement between results in the liquid and in the gaseous states provides further confirmation of the Debye theory. The values for ethyl bromide are less satisfactory than those for the other substances, as the great variation

[4] Sänger, *Physik. Z.*, **27**, 556 (1926).

of P_2 with c_2 in the dilute region makes difficult the extrapolation to $c_2 = 0$ thereby causing some inaccuracy in P_∞ and in the results derived from the P_∞ curves. As a very small variation in the drawing of the $P_\infty T$–T curves causes a considerable variation in the values of a, the values obtained for P_A cannot be regarded as exact although the value 5.8 for chloroform agrees with the difference, 6.0, between P_E and the polarization of the solid in the tabulation of Ebert.[5] a and P_A for ethyl bromide are probably too high as a result of the difficulties which have been discussed. The values of the moments agree roughly with those calculated by one of the authors[6] by a very approximate method from data on the pure liquids: $\mu \times 10^{18}$ for C_6H_{14}, 0; $CHCl_3$, 1.25; C_6H_5Cl, 1.42; C_2H_5Br, 1.56. In view of the necessary disregard of P_A and the impossibility of taking accurate account of the orienting effects of the molecules upon one another in these old calculations, the agreement of their results with the accurate values of the present work is better than would be expected.

In conclusion, it may be stated that a new, though somewhat inaccurate, method has been employed to obtain the value of P_A, the polarization due to the shifts of atoms and groups of atoms within the molecule, that accurate values have been obtained for the electric moments of molecules by measuring not merely the concentration variation but also the temperature variation of the dielectric constants and densities of liquid mixtures, and that the validity of the Debye equation as applied to liquids at infinite dilution has been established.

[5] Ebert, *Z. physik. Chem.*, **113**, 1 (1924).

[6] Smyth, **46**, 2151 (1924).

ACKNOWLEDGMENT

I wish to express my sincere thanks to Professor Charles P. Smyth for suggesting this research, and for his assistance and advice during the course of the work.